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Publication Title:

Improvements in and relating to the sterilisation of liquids

Abstract:

Abstract of GB353409

353,409. Purifying liquids. KRAUSE, G. A., 9, Bavariaring, Munich, Germany. Feb. 21, 1930, No. 5882. Convention date, March 1, 1929. [Class 46.] Liquids, especially water, are sterilized by adding thereto salts of oligodynamically active metals in small amount, not exceeding 2 mgms. of metal per litre, and leaving the liquid for sufficient time after the mixing to allow the sterilization to be completed before drawing it off for use. The time for which the liquid is held is longer as the amount of the salt added is decreased. Salts of silver, copper or mercury may be used. The metal may be removed and recovered from the treated liquid, e.g. by deposition on a grid or filter of a baser metal such as iron or aluminium, a corresponding amount of which goes into solution, or by absorp- tion, or electrochemical means. Where water is sterilized and is then treated with lime, the presence of salts of iron and aluminium, when added by the metal-recovery step, will be of use in the coagulation process. The apparatus used in sterilizing must not contain a metal baser but may contain one the same as or nobler than that in the sterilizing salt. The apparatus may be constructed of glass, stone- ware or other non-metallic material. The treat- ment may be combined with oligodynamic steriliza- tion by the aid of a free metal which must not be less noble than that in the salt added. In the example given, water, which may have been filtered, flows in through a pipe a to a vessel d where a solution of the sterilizing salt, such as silver nitrate or copper sulphate, of known strength pre- pared in a vessel b is added in accurately measured quantity through a pipe c. The water then enters chamber f through which it takes three hours to flow, the chamber being subdivided by partitions or by fillers which may be coated with a suitable metal to increase the sterilizing action. The steril- ized water passes to a vessel i which contains a grid or filter k formed of iron wire netting or iron clippings or turnings. The purified water leaving at l may be further treated with lime and filtered. The sterilizing salt may alternatively be added in solid form. Specification 325,796, [Class 46, Filtering &c.], is referred to.

PATENT SPECIFICATION

Convention Date (Germany): March 1, 1929.

353,409

Application Date (In United Kingdom): Feb. 21, 1930. No. 5882/30.

Complete Accepted: July 21, 1931.

COMPLETE SPECIFICATION.

Improvements in and relating to the Sterilisation of Liquids.

I, GEORG ALEXANDER KRAUSE, of 9, Bavariaring, Munich, Germany, a German citizen, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the sterilisation of liquids of all kinds, such as for example water, with the aid of metallic salts.

The sterilising action of certain metallic salts, such as those of silver, mercury and copper, is known; but these have not hitherto found application in practice for sterilising water. The reason for this is to be sought in that certain preliminary conditions, rendered necessary by the nature of the said salts, have not hitherto been recognised and fulfilled. Up to the present, the practical application of the sterilising metallic salts has been opposed by the following properties which they exhibit:—

1). In larger amounts, the salts have also a toxic action on the macro-organism. When the concentrations hitherto considered, in the scientific literature, to be necessary for producing the sterilising effect, are employed, the sterilised water contains an amount of metal which cannot remain harmless to the habitual consumer. Apart from the noxious effect, however, the metallic salts impart to the liquid other properties which detract from its enjoyment, in that they alter the appearance and flavour of the liquid. Thus, for example, silver nitrate, even in comparatively weak concentrations, gives water a disagreeable bitter flavour, and copper sulphate produces a blue tinge which makes the water unappetising.

Moreover, in sterilising on a large, technical scale, the employment of the metallic salts in the concentrations hitherto proposed, would entail a considerable consumption of such salts, a point which is all the more important seeing that some of them are salts of valuable metals.

2). The action of the sterilising metallic salts is not immediate, like the action of chlorine or ozone for example, but takes a fairly long time, depending, on the one hand, on the germ content of the water, and, on the other, on the concentration of the salts themselves. This fact has not hitherto been taken into consideration; but unless that be done, there is no guarantee that the germs present in the water under treatment have been destroyed.

3). The metallic salts in view, so far as they are salts of noble metals, are sensitive to the presence of base metals. If a solution of a copper salt be brought into contact with metallic iron, the copper, as is well known, separates out, as cementation copper, and iron passes into solution in its place. This fact has also been disregarded hitherto, and therefore it was impossible to obtain a satisfactory sterilising effect in the usual apparatus, which, even if not wholly constructed of base metals, nevertheless contained fittings of iron and the like, because the effective metals were already deposited from solution before they could produce their full effect.

This inconvenience naturally becomes more apparent in proportion as the concentration of the salts is weaker.

The present invention indicates the manner in which metallic salts with sterilising properties can be utilised for the sterilisation of water on a large scale, despite their aforesaid deterrent properties, and in such a way as to preclude all danger to the consumer and prevent any deterioration in the flavour or other characteristics of the water, whilst assuring economical consumption of metal.

I have found that exceedingly low concentrations of salts of oligodynamically active metals, that is to say concentrations not exceeding about 2 mgrms of metal per litre of liquid possess a relatively very powerful sterilising action; that is to say, the sterilising effect of very low concentrations is far greater, per unit amount of the active metal, than the effect of the stronger concentrations hitherto prescribed. I have, however, definitely ascertained that, in this case also, the time factor must be taken into consideration, namely that the length of time allowed for the sterilising

operation must vary inversely with the concentration employed. This necessary condition can be explained by the following hypothetical consideration. Even in extremely weak, "oligodynamic" solutions of a metallic salt (for example, a silver nitrate solution containing 10γ of Ag per litre), such a large number of metal ions are still present that, even if the water contains several hundred thousand bacteria per cubic centimetre, there are several million metal ions to each bacterium. Hence, considered in the absolute, there is always present a huge excess of active sterilising substance. Naturally, however, in the case of a stronger solution of the metallic salt, there is a greater probability that, in a given time, each bacterium will encounter a number of metal ions sufficient for its destruction. The more dilute the solution of the metallic salt, the slighter the probability of this encounter occurring in a predetermined time, and therefore, in proportion as the concentration selected is weaker, a longer interval of time must be allowed in order to obtain the same degree of certainty. I have, however, ascertained that the values of the concentration of the metallic salts and the period required for sterilisation are by no means directly in inverse proportion. If a given number of coli bacteria are killed in 10 minutes by a silver nitrate solution containing 10 mgrms. of Ag per litre, the time required with a solution a thousand times weaker (10γ of Ag per litre) will not be about a thousand times longer (i.e. about 170 hours) but only about twenty-fold (some 3 hours).

Accordingly, the essential characteristic of the present invention consists in employing, for the sterilisation of liquids, extremely low concentrations of salts of oligodynamically active metals, that is to say concentrations not exceeding about 2 mgrms of metal per litre of liquid, and at the same time leaving the liquid to stand for a sufficient time, after mixing with the metallic salt, to ensure that sterilisation is complete before the liquid is drawn off for use. In the case of stagnant liquids, all that is necessary is to leave them for the prescribed time in suitable receptacles. In the case of running liquids the interposition of a prescribed sterilisation period is synonymous with the interposition of sterilising chambers, with a cubical content sufficient, in view of the hourly volume of flow of the liquid, to ensure that each particle of the liquid takes at least the prescribed length of time to pass through the chamber.

As already mentioned, the solutions of the sterilising salts are sensitive to contact with such metals as are of baser nature than the metals of said sterilising salts. This inconvenience is naturally the more perceptible when extremely low concentrations of the metallic salts are employed, in accordance with the present invention. The inventor therefore prescribes that the parts of the vessels and apparatus in which the liquid is stored in, or passed through, during the sterilising process, must not contain any metal of baser character than the metal of the sterilising salt. Such parts of the apparatus may, for example, be constructed of glass, stoneware, or the like non-metallic material, but they may also be of the same metal as that of the sterilising salt, or of a still more noble metal; for example, sterilisation with the aid of copper sulphate may be conducted in a vessel of copper or silver. The presence of such metallic surfaces as have an oligodynamic effect themselves, is even desirable, since they assist the sterilisation. Consequently, within the scope of the present invention, the sterilisation chamber may be subdivided by oligodynamic metals, or by inserted bodies coated with such metals, so that the action of the metallic surfaces is additive to the action of the dissolved metallic salt. According to the present invention, the sterilisation with the aid of salts can be combined, in any convenient manner whatsoever, with the true "oligodynamic" sterilisation by the aid of free metals, provided only that the aforesaid rule be observed that the free metal must not be less noble than the metal of the sterilising salt.

The specified prescription for the exclusion of any base metal during the entire sterilisation period constitutes an essential feature of the present invention, since, unless this prescription be observed, the minute quantities of metal present in the solution will be precipitated by the base metal before they can exert their sterilising action.

The invention is also applicable to beer, fruit juices, milk, mineral waters and the like alimentary liquids but in regard to the application of the aforedescribed process to such liquids, I declare that I am aware of the Public Health (Preservatives, etc. in Food) Regulations, 1925—27 (Statutory Rules and Orders, 1925, No. 775, as amended by 1926, No. 1557, and 1937, No. 577) and insofar as this invention relates to the sterilisation of alimentary liquids for sale in the United Kingdom as hereinbefore described, I make no claim to the use of the invention in contravention of the law.

In itself, the employment of extremely small amounts of metallic salts affords a

certain guarantee that the purified water is uninjurious to man, and that its appearance and flavour are not impaired. Still, the human palate is extremely sensitive to the taste of silver nitrate (for example), so that it is possible that even such a small amount as 100γ of Ag per litre, in the form of silver nitrate, may be found disagreeable. Moreover, it is desirable, for reasons of economy, that the metals—some of which are valuable—of the sterilising salts should be recovered after the sterilisation is completed.

In carrying out the invention, therefore, there is disposed, beyond the sterilisation chamber, an apparatus of any convenient kind in which the valuable metals are retained. This retention of the metals can be effected by adsorption on substances of large superficial area, or by electrochemical means, or in any other suitable way. For example, a grid or filter, composed of or coated with a metal of baser character, than the metal of the sterilising salt, is provided in rear of the sterilising chamber. In sterilising with salts of silver, mercury, or copper, the filter can be equipped with iron or aluminium. The noble metals will then be deposited on the collector, and a corresponding amount of the base metal—iron or aluminium—will pass into solution. The presence of these metals in the purified water will not injure the consumer, especially since they are in the same exceedingly weak degree of concentration as the sterilising salts were previously. If, as is customary in many localities, the water is treated with lime after sterilising, the presence of the salts of iron or aluminium will even have a favourable influence on the coagulation process, in which larger amounts of salts of iron or aluminium are intentionally added to the water.

The features of the invention may be summarised as follows:—

The practical application of metallic salts for the sterilisation of liquids, especially potable water, is rendered possible by the new prescription that the sterilising salts are used in extremely weak concentrations as hereinbefore set forth; that, after the addition of the salts, sufficient sterilisation periods are allowed; that any metal of baser character than the metal of the sterilising salt is kept out of the sterilising chamber, and that, after their action has terminated, the metals are extracted from the solution by a collecting apparatus and recovered.

The advantages of the process are:—economical management of the valuable metal; certainty of obtaining the desired sterilising effect, and the production of an absolutely innocuous and palatable pure liquid.

An apparatus for use in carrying out the invention is diagrammatically illustrated by way of example in the accompanying drawing.

The impure water, which in some cases has already been filtered, flows through the pipe *a* with an hourly volume determined by the pump output. A solution of the sterilising salt, such as silver nitrate, or copper sulphate, of known strength, is prepared in the solution vessel *b*. This solution is drawn from the vessel, through the pipe *c*, in accurately measured quantity in relation to the hourly volume of the water, and is mixed with the flow of the latter in *d*. The mixture enters at *e* into the auxiliary sterilising chamber *f*, which for a volume of 1000 cu. metres per hour, has a capacity of 3000 cu. metres, so that each particle of water takes 3 hours to flow through the chamber. The sterilising vessel can be constructed of non-metallic material, such as glass, concrete or the like, It may also be made of, or lined with, a metal which is not of baser character than the metal contained in the sterilising salt. The auxiliary sterilising chamber can also be subdivided by means of partitions *g* or other members, or by means of any convenient form of fillers, which, for the purpose of increasing the sterilising action, may consist of, or be coated with, a suitable metal. The sterilised water escapes through the overflow *h* to the collecting apparatus *i*. This contains, as its substantial component, a grid or filter *k*, consisting, for example, of iron wire netting. The collecting apparatus may also consist, alternatively, of a vessel in the form of a tower, filled with iron clippings or turnings. The purified water issues from the collector at *l*. If necessary, a coagulation treatment with lime, and filtration, follow before the water is passed on to the consumer.

It should be well understood that the arrangement represented in the diagrammatic drawing is given solely by way of example and that various other arrangements can be employed for carrying out the process. In particular, there is no need for the sterilising salt to be incorporated with the current of liquid to be sterilised in the form of a saturated or conveniently diluted solution. On the contrary, it also comes within the scope of the invention to drop the solid salt into the liquid, in which event it is, of course, necessary to provide means for ensuring the accurate maintenance of the desired concentration.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to

be performed, I declare that I am aware of my Specification No. 325,796 of prior date to my present application but published subsequently thereto and I make no claim to anything contained in my said prior specification, but that what I claim is:—

1). A process of sterilising liquids with the aid of salts of oligodynamically active metals, characterised in that said salts are added to the liquid to be sterilised in extremely low concentrations, not exceeding about 2 m. grms. of metal per litre of the liquid and that between this operation and the widthdrawal for consumption, a period of time commensurate with the smallness of the amount of metallic salt employed is allowed to elapse for completing the process of sterilisation.

2). Process as set forth in claim 1, in which, after the incorporation of the sterilising salt and up to the close of the period prescribed for the sterilisation, the liquid is not brought into contact with any metal of a baser character than the metal of the sterilising salt.

3). Process as set forth in claims 1 and 2, in which, after the sterilising process is completed, the liquid is passed through an apparatus in which the metal of the sterilising salt is retained.

4). The process of and apparatus for sterilising liquids by means of metallic salts substantially as described with reference to the accompanying drawing.

Dated this 21st day of February, 1930.

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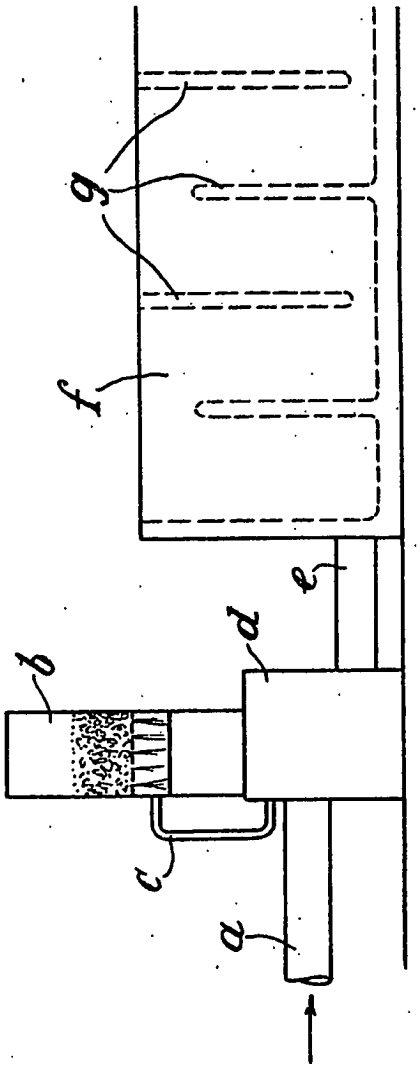

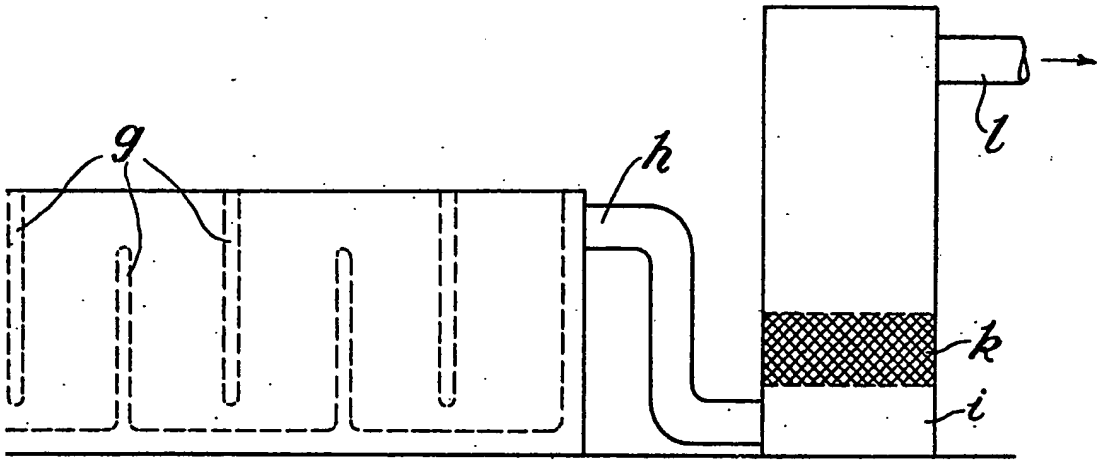

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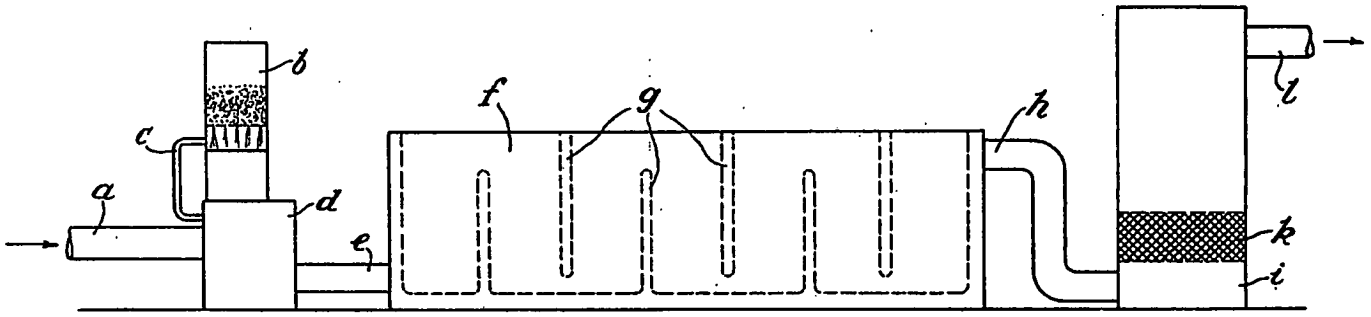

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